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Stack Sampling Technical Information
A Collection of Monographs and Papers
Volume I

(U.S.) Environmental Protection Agency
Research Triangle Park, NC

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"Stack Sampling Technical Information" is a four-volume collection of monographs and papers which have been compiled by the Emission Measurement Branch, ESED, OAQPS. The information specifically relate to current EPA test methods and compliance test procedures. The data presented in some of these documents have served as the basis for a number of revisions made in the EPA Reference Methods 1 through 8. Several of the documents are also useful in determining acceptable alternative procedures.

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A Collection of Monographs and Papers

Volume I

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Stack Sampling Technical Information
A Collection of Monographs and Papers
Volume I

Emission Standards and Engineering Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air, Noise, and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

October 1978

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PREFACE

The Clean Air Act of 1970 requires the Administrator of the Environmental Protection Agency to establish national emission standards for new stationary sources (Section 111) and hazardous air pollutants (Section 112). The development of these emission standards required the concurrent development of reference test methods and procedures. The reference test methods and procedures are published in the Federal Register along with the appropriate regulations.

From time to time, questions would surface concerning the methods and procedures. In many cases, specific studies would be needed to provide informed, objective answers. The papers and monographs resulting from these studies were usually distributed to people involved in emission measurement; a major method of distribution has been the Source Evaluation Society Newsletter.

To provide a readily available resource for new and experienced personnel, and to further promote standardized reference methods and procedures, it has been decided to publish the papers and monographs in a single compendium. The compendium consists of four volumes. The Table of Contents for all four volumes is reproduced in each volume for ease of reference.

Congratulations and sincere appreciation to the people who did the work and took the time to prepare the papers and monographs. For the most part the work was done because of personal commitments to the development of objective, standardized methodology, and a firm belief that attention to the details of stack sampling makes for good data. The foresight of Mr. Robert L. Ajax, the former Chief of the Emission Measurement Branch and now the Assistant Director, Emission Standards and Engineering Division, in providing the atmosphere and encouragement to perform the studies is gratefully acknowledged. The skill and dedication of Mr. Roger Shigehara, in providing personal supervision for most of the work, is commended.

Don R. Goodwin
Director
Emission Standards and
Engineering Division

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METHOD FOR CALCULATING POWER PLANT EMISSION RATE

By

R. T. Shigehara, R. M. Neulicht,* and W. S. Smith**

Introduction

In the final State Implementation Plans submitted by all 50 States, the District of Columbia, Puerto Rico, American Samoa, Guam, and the Virgin Islands in response to the 1970 Clean Air Act, most of the regulations for the control of particulate, sulfur dioxide, and nitrogen oxide emissions from fuel burning sources are expressed in pounds of emissions per million Btu of heat input ($lb/10^6$ Btu)[1]. The Federal New Source Performance Standards[2] regulating the same pollutants from fossil fuel-fired steam generating units of more than 250 million Btu/hr heat input are expressed in the same terms. To arrive at this expression, the Federal perfromance standard regulations call for the determination of the pollutant concentration (C), the effluent volumetric flow rate (Q_s), and the heat input rate (Q_H). In addition, the heat input rate must be confirmed by a material balance over the steam generator system.

The purpose of this paper is to present an alternative method for arriving with improved accuracy at the expression of $lb/10^6$ Btu called for by the State and Federal regulations without having to determine effluent gas volumetric flow rate, fuel rate, or fuel heat content.

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** Entropy Environmentalists, Inc.

Derivation of the F-Factor Method

Standard Method

In the standard method of calculating emission rates:

$$E = \frac{C\ Q_S}{Q_H} \qquad (1)$$

where: E = pollutant emission, $lb/10^6$ Btu.

C = pollutant concentration, dry basis, lb/scfd.

Q_S = dry effluent volumetric flow rate, scfd/hr.

Q_H = heat input rate, 10^6 Btu/hr.

F-Factor Method

When the laws of conservation of mass and energy are applied, the following must hold true:

$$\frac{Q_S}{Q_H}\left(\frac{20.9 - \%O_2}{20.9}\right) = \frac{V_S}{HHV} \qquad (2)$$

where: V_S = theoretical dry combustion products per pound of fuel burned, scfd/lb.

HHV = high heating value, 10^6 Btu/lb.

$\frac{20.9 - \%O_2}{20.9}$ = excess air correction factor.

Solving Equation 2 for the ratio Q_S/Q_H and substituting into Equation 1 yields:

$$E = C\left(\frac{V_S}{HHV}\right)\left(\frac{20.9}{20.9 - \%O_2}\right) \qquad (3)$$

The amount of dry effluent gas (V_s) generated by combustion of a fossil fuel can easily be calculated from the ultimate analysis. The high heating value can be obtained from standard calorific determinations. The ratio, F, between V_s and HHV can be calculated for various fossil fuels; F is the effluent gas generated per 10^4 Btu heat content:

$$F = \frac{V_s}{HHV\ (100)} \qquad (4)$$

Values for F calculated from data obtained from the literature are summarized in Table I. Of course, this ratio can be calculated for each specific case, but the dry effluent per 10^4 Btu varies no more than about $\pm$ 3%. For this reason, these ratios will be considered as constants and will hereafter be called "F Factors." The use of these F Factors, as will be discussed later, eliminates the need for ultimate and calorific analyses. A list of average F Factors derived from Table I is shown in Table II.

Table I

F Factors for Fossil Fuels
(Calculated from Data
in Literature)

Fuel	Lit. Source	Samples, No.	Avg., 10^4 scfd/10^6 Btu[a]	Max Dev. (+)	Max Dev. (-)
Coal					
Anthracite	3	3	101.0	2.4	1.2
	4	1	102.8	-	-
Total or avg.		4	101.4	2.0	1.6
Bituminous	3	8	97.5	1.4	1.1
	5	44	97.5	2.1	2.4
	6	38	98.7	1.4	1.2
	7	13	98.9	1.5	1.1
	8	39	98.6	2.3	1.4
	9	26	98.2	2.1	1.2
	10	57	98.0	1.0	1.2
	4	1	99.3	-	-
Lignite	3	1	97.5	-	-
	5	2	99.4	1.0	1.0
Total or avg.		229	98.2	2.7	3.1
Oil					
Crude	11,12	6	91.9	1.9	2.6
	4	1	92.0	-	-
Residuum	12	4	93.1	1.9	2.1
Distillate	12	2	92.7	0.5	1.5
Fuel	11	3	91.5	1.9	1.3
Total or avg.		16	92.2	2.8	3.0
Gas					
Natural	4	1	88.0	-	-
	13	4	86.7	0.3	0.5
Commercial propane	13	2	86.8	0.1	0.1
Commercial butane	13	2	89.0	0.3	0.3
Total or avg.		9	87.4	2.2	1.2

[a]Standard conditions are 70°F, 29.92 in. Hg, and 0% excess air.

Table II. Average F Factors[a]

Fuel	F Factors scfd/10^4 Btu[b]
Coal-anthracite	101.4
Coal-bituminous, lignite	98.2
Oil-crude, residuum, distillate, fuel oil	92.2
Gas-natural, butane, propane	87.4

[a]Derived from Table I.

[b]70°F, 29.92 in. Hg., and 0% excess air.

Use of F Factors

Emission Rate Calculation

When Q_S and Q_H are not measured or are unobtainable, F Factors can be used to calculate E. Substituting Equation 4 into Equation 3 we obtain:

$$E = C\ F\ \left(\frac{2090}{20.9 - \%O_2}\right)$$

where: F = F Factor from Table II, in scfd/10^4 Btu.

Equation 5 shows that E can be obtained by simply measuring the pollutant concentration and percentage oxygen and by knowing the type of fuel being burned. Q_S and Q_H are no longer required.

Material Balance Check

If Q_S and Q_H are measured, F Factors can be used to check sampling data by comparing them with F_m.

where:

$$F_m = \frac{Q_S}{Q_H}\left(\frac{20.9 - \%O_2}{20.9}\right)$$

Fuel Analysis Check

If ultimate and proximate analyses are made, F Factors can be used to check the accuracy of such analyses by comparing them with V_s/HHV which is the calculated amount of dry effluent gas generated per 10^4 Btu heat content.

Discussion

In the present method for calculating power plant emission rates, four separate quantities must be determined, each of which requires at least two measurements, as shown in Table III.

Table III

Quantities and Measurements Required
For Calculation of Power Plant
Emission Rates (Regulation Method)

Quantity Used	Quantity Measured
1. Pollutant concentration, C	a. Pollutant mass b. Dry gas volume
2. Effluent volumetric flow rate, Q_s	a. Velocity head b. Stack temperature c. Stack pressure d. Dry gas composition (Orsat) $\%CO_2$, $\%O_2$, $\%N_2$ e. Moisture content (determined during measurement of 1 (b))
3. Heat input rate, Q_H	a. Coal input rate b. Calorific analysis of coal
4. Material balance confirmation	a. Effluent volumetric flow rate (determined in 2(a-e)) b. Ultimate analysis of coal c. Excess air (calculated from 2(d))

From Table III, it is obvious that the use of F Factors in calculating E requires fewer measurements than are required by methodology in current use. Because there are fewer measurements, the inaccuracies attendant to measuring items 2 through 4 (except for 2d) are not included in the final results. Granted that those measurements in 2 must be made for isokinetic sampling, but the errors made do not contribute directly to the emission standard calculation.

Conclusion

It has been shown that, for a given type of fuel, a relationship exists between the fuel heat value and dry effluent that permits a constant (F Factor) to be calculated within $\pm$ 3% deviation.

This implies that: (1) pollutant emissions in $lb/10^6$ Btu can be easily calculated when only pollutant concentration, O_2 concentration, and fuel type are known, thus eliminating the need for measuring effluent volumetric flow rate and heat input rate; (2) the inconsistencies that arise in measuring the heat input rate are eliminated while at most a maximum error of 3% may be propagated from the F Factor to the pollutant emission rate; and (3) if effluent volumetric flow rate (Q_s) and heat input rate (Q_H) are measured, an F_m Factor can be calculated from those values and compared with the F Factor as a mass balance check.

In short, use of the F Factor provides a method less complex than the one now employed for calculating power plant emission rates and evaluating the sampling data.

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EMISSION CORRECTION FACTOR for FOSSIL FUEL-FIRED STEAM GENERATORS
CO_2 CONCENTRATION APPROACH

Roy Neulicht*

Introduction

The Federal Standards of Performance for New Stationary Sources regulating particulate matter, sulfur dioxide, and nitrogen oxide emissions from fossil fuel-fired steam generating units of more than 63 million kcal/hr (250 million Btu/hr) heat input are expressed in terms of mass per unit of heat input, $g/10^6$ cal ($lb/10^6$ Btu). To arrive at this emission rate, the existing method[1] requires determination of the pollutant concentration (C), the effluent volumetric flow rate (Q_s), and the heat input rate (Q_h). An F-Factor approach requiring determination of the fuel type, pollutant concentration (C), and the oxygen concentration ($\%O_2$) has been proposed[2] as the reference method to replace the existing method.

The purpose of this paper is to present a third method, based on the F-Factor approach and employing a dilution correction factor based on measuring the carbon dioxide rather than oxygen concentration. This method, which will be called the F_c-Factor method,is based on two facts:

1. The comparison of the theoretical carbon dioxide produced during combustion to the measured carbon dioxide provides an exact basis for dilution correction.
2. Within any fossil fuel type category, the ratio of the volume of carbon dioxide to the calories released is essentially a constant.

The method has two advantages:

1. Emission rates may be determined from wet basis concentration measurements without recalculation of the F_c-Factor.

* Emission Measurement Branch, ESED, OAQPS, EPA, RTP, NC
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2. Use of CO_2 for correcting for dilution provides flexibility by providing an additional method for determining emission rates; for example, in some cases measuring CO_2 may be more convenient than measuring O_2.

One disadvantage of the CO_2 correction factor is that it cannot be used after control devices that alter the CO_2 concentration (e.g., wet scrubbers that remove CO_2) or in situations where CO_2 is added.

Derivation of F_c-Factor Method

The method calculating emission rates as promulgated in the Federal Register[1] is:

$$E = C \frac{Q_s}{Q_H} \qquad (1)$$

where: E = pollutant emission, $g/10^6$ cal ($lb/10^6$Btu)

C = pollutant concentration, dry basis, g/dscm, (lb/dscf)

Q_s = dry effluent volumetric flow rate, dscm/hr (dscf/hr)

Q_H = heat input rate, 10^6 cal/hr (10^6 Btu/hr)

When the laws of conservation of mass and energy are applied, the following must hold true:

$$\frac{Q_s}{Q_H}\left(\frac{\%CO_{2m}}{\%CO_{2t}}\right) = \frac{V_t}{HHV} \qquad (2)$$

where: V_t = total theoretical dry combustion products per unit mass of fuel burned, dscm/g (dscf/lb)

HHV = high heating value, 10^6 cal/g (10^6 Btu/lb)

$\frac{\%CO_{2m}}{\%CO_{2t}}$ = dilution correction factor, ratio of measured carbon dioxide and theoretical carbon dioxide produced from combustion, dry basis

Solving Equation 2 for the ratio Q_s/Q_H and substituting into Equation 1 yields:

$$E = C\left(\frac{V_t}{HHV}\right)\left(\frac{\%CO_{2t}}{\%CO_{2m}}\right) \qquad (3)$$

Substituting $\frac{V_c}{V_t}$ (100) for $\%CO_{2t}$ yields:

$$E = C\left(\frac{V_t}{HHV}\right)\left(\frac{1}{\%CO_{2m}}\right)\left(\frac{V_c}{V_t}\right)(100) \qquad (4)$$

where: V_c = theoretical volume of carbon dioxide produced per unit mass of fuel burned, scm/g (scf/lb)

Elimination of V_t from Equation 4 and rearrangement yields:

$$E = C\left(\frac{100}{\%CO_{2m}}\right)\left(\frac{V_c}{HHV}\right) \qquad (5)$$

or

$$E = C\left(\frac{100}{\%CO_{2m}}\right)(F_c) \qquad (6)$$

where: $F_c = \frac{V_c}{HHV}$, the ratio of theoretical CO_2 generated by combustion to the high heating valve of the fuel combusted, scm/10^6 cal (scf/10^6 Btu).

The high heating value of the fuel combusted can be obtained from

standard calorific determinations. The amount of theoretical carbon dioxide generated by combustion can easily be calculated from the ultimate analysis. The ratio, F_c, has been calculated for various fossil fuels from data obtained from the literature; these calculated ratios are summarized in Table I. For any fuel type, the ratio is found to be a constant with a maximum deviation of $\pm$ 5.9%. Average F_c - Factors for each fuel type are given in Table II.

Note that Equation 6 for the determination of the pollutant emission rate (E) has been developed in terms of dry measurements. However, it is a simple matter to show that wet basis measurements may be used. Given Equation 6 and multiplying both the measured pollutant concentration (C) and the measured carbon dioxide concentration ($\%CO_{2m}$) by the dry mole fraction (D) of the effluent gas yields:

$$E = [(C)(D)] \left[\frac{100}{(\%CO_{2m})\ (D)} \right] F_c \qquad (7)$$

or

$$E = C_w \left(\frac{100}{\%CO_{2w}} \right) F_c \qquad (8)$$

where: C_w = pollutant concentration, wet basis, g/scm (lb/scf)

$\%CO_{2w}$ = measured concentration of carbon dioxide, wet basis, (expressed as percent).

Equations 6 and 8 show that, using the average F_c - Factor approach, the pollutant emission rate (E) can be obtained by simply knowing the type of fuel burned and measuring the pollutant and carbon dioxide concentrations

on either a wet or dry basis.

Determination of F_c - Factor

Rather than use an average F_c - Factor, the F_c - Factor can be determined on an individual case-by-case basis. As already stated, the high heating value of the fuel is determined from standard calorific determinations. The theoretical carbon dioxide generated by combustion is easily calculated from the following equations based on stoichiometry[3] and on information from an ultimate fuel analysis:

$$V_c = 0.200 \times 10^{-4} \; \%C \; \frac{\text{scm } CO_2}{\text{g fuel}} \qquad (9)$$

or

$$V_c = 0.321 \; \%C \; \frac{\text{scf } CO_2}{\text{lb fuel}} \qquad (10)$$

where: %C= percent carbon by weight determined from ultimate analysis.

Given the definition of the F_c - Factor,

$$F_c = \frac{V_c}{HHV} \qquad (11)$$

and substituting Equations 9 and 10 yields:

$$F_c = \frac{0.200 \times 10^{-4} \; \%C}{HHV} \quad \text{for metric units of } \text{scm}/10^6 \text{ cal} \qquad (12)$$

and

$$F_c = \frac{0.321 \; \%C}{HHV} \quad \text{for English units of } \text{scf}/10^6 \text{ Btu} \qquad (13)$$

Note: %C and HHV must be on a consistent basis, e.g., if %C is determined on an as-received basis, HHV must also be on an as-received basis.

Conclusion

It has been shown that, for a given fuel type, a relationship exists between the fuel calorific value and the theoretical effluent carbon dioxide, which permits an average F_c - Factor to be calculated within $\pm$ 5.9% deviation. This provides a method for calculating power plant emission rates that may be used when the pollutant concentration, carbon dioxide concentration, and fuel type are known. The equation for such a calculation is given as follows:

$$E = C\ F_c\left(\frac{100}{\%CO_2}\right) \qquad (14)$$

where: E = pollutant emission, g/10^6 cal (lb/10^6 Btu)

C = pollutant concentration, g/scm (lb/scf)

$\%CO_2$ = carbon dioxide content by volume (expressed as percent)

F_c = a factor representing a ratio of the volume of theoretical carbon dioxide generated to the calorific value of the fuel combusted.

Note: C and $\%CO_2$ may be measured either on a wet or dry basis provided that the same basis is used for each.

Furthermore, average values of F_c are given for each fossil fuel type, and the necessary equations for determining the F_c - Factor on a case-by-case basis are presented.

TABLE I. F_c - FACTOR FOR FOSSIL FUELS

Fuel Type	Literature Source	Number of Samples	Average $\frac{scm^a CO_2}{10^6 \text{ cal}}$	Max. Dev.,% +	Max. Dev.,% -
Coal					
Anthracite	4	3	0.2202		
	5	1	0.2292		
	6	3	0.2218		
Average			0.2222	4.1	4.1
Bituminous	6	13	0.2029		
	7	39	0.2032		
	8	15	0.2065		
	9	46	0.2025		
	10	41	0.2022		
	11	58	0.2011		
Lignite	6	1	0.2105		
	4	1	0.2123		
Average			0.2027	5.9	5.2
Oil					
Crude	5	1	0.1585		
	12	6	0.1591		
Residium	12	4	0.1655		
Distillate	12	2	0.1610		
Average			0.1613	5.1	2.2
Gas					
Natural	13	4	0.1160		
	4	3	0.1180		
Average			0.1168	3.9	2.0
Propane	13	2	0.1351		
Average			0.1351	1.0	1.0
Butane	13	2	0.1420		
Average			0.1420	1.0	1.0

[a]Standard conditions are 70°F, 29.92 in. Hg, and 0% excess air.

TABLE II. AVERAGE F_c - FACTORS

Fuel Type	scm[a] $CO_2/10^6$ cal	scf[a] $CO_2/10^6$ Btu
Coal		
Anthracite	0.222	1980
Bituminous and lignite	0.203	1810
Oil	0.161	1430
Gas		
Natural	0.117	1040
Propane	0.135	1200
Butane	0.142	1260

[a]Standard conditions are 70°F, 29.92 in. Hg, and 0% excess air.

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DERIVATION OF EQUATIONS FOR CALCULATING POWER PLANT EMISSION RATES

O_2 Based Method - Wet and Dry Measurements

R. T. Shigehara & R. M. Neulicht*

INTRODUCTION

The Federal New Source Performance Standards[1] regulating particulate matter, sulfur dioxide, and nitrogen oxides emissions from fossil fuel-fired steam generating units are expressed in terms of mass emissions per unit of heat input. Shigehara et al.[2] developed a means of determining the emission rates in the desired terms using stoichiometric factors and oxygen (O_2) measurements. This procedure is expressed in equation form as follows:

$$E = C\ F\ \left(\frac{20.9}{20.9 - \%O_2}\right) \qquad (1)$$

where: E = emission rate, $lb/10^6$ Btu

C = pollutant concentration, lb/scf

F = fuel stoichiometric factor, $scf/10^6$ Btu

$\%O_2$ = O_2 concentration, percent.

Initially, the above expression has been applied only to dry (moisture free) based measurements. However, because some automatic instruments are capable of determining carbon (C) and $\%O_2$ on a wet basis, questions have been asked about the derivation of Equation 1 and how wet based measurements affect the equation. The derivation of the equations for wet and dry based measurements and a list of average F-factors are presented in this text.

DERIVATION OF EQUATIONS

The basic equation for calculating emission rate is given by:

$$E = \frac{C\ Q_s}{Q_H} \qquad (2)$$

* Emission Measurement Branch, ESED, OAQPS, EPA, July 1976

where: Q_s = effluent volumetric flow rate, scf/hr

Q_H = heat input rate, 10^6 Btu/hr.

The product of C and Q_s is simply the mass rate; thus, both C and Q_s must be determined on a consistent basis, i.e. either wet or dry. To distinguish between wet and dry based measurements, the subscripts "w" and "d", respectively, will be used.

Dry Basis

If E is calculated from dry based measurements, Equation 2 becomes:

$$E = \frac{C_d \, Q_{sd}}{Q_H} \tag{3}$$

Q_{sd} can be written as:

$$Q_{sd} = S_d + EA_d \tag{4}$$

where: S_d = dry volumetric flow rate of effluent at stoichiometric conditions, dscf/hr

EA_d = dry volumetric flow rate of excess air in the effluent, dscf/hr.

An adjustment factor, A_d, which when multiplied by Q_{sd} would adjust it to dry stoichiometric conditions, S_d, can be derived as follows:

$$Q_{sd} \, A_d = S_d = Q_{sd} - EA_d \tag{5}$$

$$A_d = 1 - \frac{EA_d}{Q_{sd}} \tag{6}$$

Since $EA_d = Q_{O_2}/0.209$, where Q_{O_2} is the volumetric flow rate of O_2 in the effluent and 0.209 is the fraction by volume of O_2 in dry air,

$$A_d = 1 - \frac{Q_{O_2}}{0.209\ Q_{sd}} \tag{7}$$

Noting that Q_{O_2}/Q_{sd} is the proportion by volume of O_2 in the dry effluent mixture (O_{2pd}) and substituting into Equation 7, A_d becomes:

$$A_d = 1 - \frac{O_{2pd}}{0.209}$$

$$= \frac{20.9 - \%O_{2d}}{20.9} \tag{8}$$

and

$$S_d = Q_{sd}\ (\frac{20.9 - \%O_{2d}}{20.9}) \tag{9}$$

Substituting Equation 9 into Equation 2 yields:

$$E = C_d \frac{S_d}{Q_H}\ \frac{20.9}{20.9 - \%O_{2d}} \tag{10}$$

The ratio, S_d/Q_H, is simply the dry effluent gas at stoichiometric conditions generated per unit of heat input and can be calculated from ultimate and calorific analyses of the fuel. These calculated ratios are defined as F_d and are summarized in Table I. Inserting $F_d = S_d/Q_H$,

Equation 10 can be rewritten in its final form as:

$$E = C_d\ F_d\ \frac{20.9}{20.9 - \%O_{2d}} \tag{11}$$

Wet Basis

If E is calculated from wet based measurements, Equation 2 becomes:

$$E = \frac{C_w Q_{sw}}{Q_H} \tag{12}$$

As before, Q_{sw} can be written as:

$$Q_{sw} = S_w + EA_w \tag{13}$$

If the combustion air is dry, then $EA_w = EA_d$ and S_w and Q_{sw} will only include moisture derived from the fuel. It follows that:

$$Q_{sw} A_w = S_w = Q_{sw} - EA_d \tag{14}$$

$$A_w = 1 - \frac{EA_d}{Q_{sw}} \tag{15}$$

$$= 1 - \frac{Q_{O_2}}{0.209\ Q_{sw}} \tag{16}$$

$$= 1 - \frac{O_{2pw}}{0.209} \tag{17}$$

$$= \frac{20.9 - \%O_{2w}}{20.9} \tag{18}$$

$$S_w = Q_{sw} \frac{20.9 - \%O_{2w}}{20.9} \tag{19}$$

$$E = C_w \frac{S_w}{Q_H} \frac{20.9}{20.9 - \%O_{2w}} \tag{20}$$

Defining S_w/Q_H as F_w,

$$E = C_w F_w \frac{20.9}{20.9 - \%O_{2w}} \tag{21}$$

To assume that combustion air is dry, however, is obviously not true. EA_w must include moisture so that:

$$EA_{wa} = \frac{EA_d}{1 - B_{wa}} \tag{22}$$

where B_{wa} is the moisture content in the ambient air; the subscript "a" is used to denote the inclusion of ambient moisture. Note also that Q_{sw} and S_w now include the moisture from the ambient air. Following steps that are similar to steps 14 through 21:

$$Q_{swa} A_{wa} = S_{wa} = Q_{swa} - EA_{wa} \tag{23}$$

$$A_{wa} = 1 - \frac{EA_{wa}}{Q_{swa}} \tag{24}$$

$$= 1 - \frac{EA_d}{Q_{swa} (1 - B_{wa})} \tag{25}$$

$$= 1 - \frac{Q_{O_2}}{0.209\ Q_{swa} (1 - B_{wa})} \tag{26}$$

$$= 1 - \frac{O_{2pwa}}{0.209\ (1 - B_{wa})} \tag{27}$$

$$= \frac{20.9\ (1 - B_{wa}) - \%O_{2wa}}{20.9\ (1 - B_{wa})} \tag{28}$$

$$S_{wa} = Q_{swa}\ \frac{20.9\ (1 - B_{wa}) - \%O_{2wa}}{20.9\ (1 - B_{wa})} \tag{29}$$

$$E = C_{wa}\ \frac{S_{wa}}{Q_H}\ \frac{20.9\ (1 - B_{wa})}{20.9\ (1 - B_{wa}) - \%O_{2wa}} \tag{30}$$

Defining S_{wa}/Q_H as F_{wa}:

$$E = C_{wa}\ F_{wa}\ \frac{20.9\ (1 - B_{wa})}{20.9\ (1 - B_{wa}) - \%O_{2wa}} \tag{31}$$

The inclusion of ambient air in F_{wa}, however, is undesirable in that it becomes a variable. Written in terms of F_w, i.e. where ambient moisture is not included, F_{wa} can be written as:

$$F_{wa} = \frac{S_{wa}}{Q_H} = \frac{S_w + \frac{ThA\ (B_{wa})}{(1 - B_{wa})}}{Q_H} \tag{32}$$

$$= \frac{S_w}{Q_H} + \frac{ThA}{Q_H}\left[\frac{B_{wa}}{1 - B_{wa}}\right] \tag{33}$$

where ThA is the theoretical air required for complete combustion. Defining, as before, S_w/Q_H as F_w, i.e. without ambient air moisture, and ThA/Q_H as F_{ThA}, i.e. theoretical air per unit of heat input, Equation 33 can be rewritten as:

$$F_{wa} = F_w + F_{ThA}\left[\frac{B_{wa}}{1 - B_{wa}}\right] \tag{34}$$

$$= F_w\left[1 + \frac{F_{ThA}}{F_w}\left(\frac{B_{wa}}{1 - B_{wa}}\right)\right] \tag{35}$$

Substituting into Equation 31 and simplifying yields:

$$E = C_{wa}\, F_w\left[1 + \frac{F_{ThA}}{F_w}\left(\frac{B_{wa}}{1 - B_{wa}}\right)\right]\frac{20.9\,(1 - B_{wa})}{20.9\,(1 - B_{wa}) - \%O_{2wa}}$$

$$= C_{wa}\, F_w\left[1 - B_{wa}\left(1 - \frac{F_{ThA}}{F_w}\right)\right]\frac{20.9}{20.9\,(1 - B_{wa}) - \%O_{2wa}} \tag{36}$$

Consider now the expression $\left[1 - B_{wa}\,(1 - F_{ThA}/F_w)\right]$. Average values of F_{ThA}/F_w are: coal = 0.960; oil = 0.948; gas = 0.914. An extreme case of ambient moisture content of 6.4% would occur at 100°F and 100% relative humidity. The expression cited above under these conditions would yield values of: coal = 0.9975;

oil = 0.9967; and gas = 0.9945. Therefore, neglecting this cited expression would introduce a positive bias of no more than o.25 to 0.55%. Understanding this, Equation 36 simplifies to its final form:*

$$E = C_{wa} F_w \frac{20.9}{20.9 (1 - B_{wa}) - \%O_{2wa}} \qquad (37)$$

Average values of F_w are listed in Table II. From Tables I and II it can be seen that F_d factors have a maximum arithmetic deviation of ± 3.1 percent and F_w factors, ± 3.8 percent.

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* This equation was originally derived by G. F. McGowan, Vice President, Environmental Technology Division, Lear Siegler, Englewood, Colorado.

Table I. AVERAGE F_d FACTORS FOR FOSSIL FUELS

Fuel type	Samples, No.	F_d dscf/10^6 Btu[a]	Max. dev., %
Coal			
Anthracite	4	10140	±2.0
Bituminous, lignite	229	9820	±3.1
Oil	16	9220	±3.0
Nat. gas, propane, butane	9	8740	±2.2

[a] Standard conditions are 70°F, 29.92 in. Hg, and 0% excess air.

Table II. AVERAGE F_w FACTORS FOR FOSSIL FUELS

Fuel type	Samples, No.	F_w wscf/10^6 Btu[a]	Max. dev., %
Coal			
Anthracite	7	10580	±1.5
Bituminous	129	10680	±2.7
Lignite	174	12000	±3.8
Oil	13	10360	±3.5
Gas			
Natural	7	10650	±0.8
Propane	2	10240	±0.4
Butane	2	10430	±0.7

[a] Standard conditions are 70°F, 29.92 in. Hg, and 0% excess air.

SUMMARY OF F FACTOR METHODS FOR DETERMINING EMISSIONS FROM COMBUSTION SOURCES

R. T. Shigehara, R. M. Neulicht, W. S. Smith,
and J. W. Peeler

INTRODUCTION

The Federal Standards of Performance for New Stationary Sources, regulating particulate matter, sulfur dioxide, and nitrogen oxide emissions from fossil fuel-fired steam generating units, are expressed in terms of pollutant mass per unit of heat input. Many State regulations for combustion equipment are expressed in the same form. To arrive at this emission rate, the original method[1] required the determination of the pollutant concentration, effluent volumetric flow rate, and heat input rate. In the October 6, 1975, Federal Register,[2] an "F Factor" technique, which required only the determination of the fuel type, pollutant concentration, and the oxygen (O_2) concentration, was promulgated as a procedure to replace the original method. At the same time, an F Factor approach, based on either O_2 or carbon dioxide (CO_2) measurements, was promulgated for use in reducing the pollutant concentration data obtained under the continuous monitoring requirements to the desired units. Recently, wet F Factors,[3] which allow the use of wet basis measurements of the same parameters, and F Factors for wood and refuse have been calculated.

The purpose of this paper is to summarize the various methods and to present the calculated F Factor values for the different types of fuels. The various uses of F Factors and errors involved in certain applications and conditions are also discussed.

SUMMARY OF METHODS

The first method, referred to simply as the F Factor Method, is based on two principles:

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1. The ratio of the quantity of dry effluent gas generated by combustion to the gross calorific value of the fuel is a constant within any given fuel category. This ratio is normally called the dry F Factor; however, for purposes of this paper, it will be called the F_d Factor.
2. An excess air correction factor may be expressed in terms of the dry oxygen content of the effluent stream.

The use of this method requires dry basis measurements of the pollutant concentration (C_d) and percent oxygen ($\%O_{2d}$). The emission rate (E) is calculated by the equation:

$$E = C_d \, F_d \left(\frac{20.9}{20.9 - \%O_{2d}} \right) \qquad (1)$$

If the moisture content of the flue gas (B_{ws}) is determined, a natural derivative of Equation 1, which would allow direct wet basis measurements of pollutant and oxygen concentrations, i.e. C_w and $\%O_{2w}$, respectively, is as follows:

$$E = C_w \, F_d \left[\frac{20.9}{20.9 \, (1 - B_{ws}) - \%O_{2w}} \right] \qquad (2)$$

This equation has been approved in principle by the Environmental Protection Agency and may be used if it is demonstrated that B_{ws} can be accurately determined and that any absolute error in B_{ws} will not cause an error of more than $\pm$ 1.5 percent in the term

$$\frac{20.9}{20.9 \, (1 - B_{ws}) - \%O_{2w}} \, .$$

The second technique, called the F_w Factor Method, is based on the same two principles as the F_d Factor Method, except that the two quantities, the effluent gas and the oxygen concentration, are determined on a wet basis. The ratio of

the quantity of wet effluent gas generated by combustion to the gross calorific value of the fuel is called the wet F Factor or the F_w Factor. The use of this technique, however, requires in addition to the wet pollutant concentration (C_w) and oxygen ($\%O_{2w}$) the determination of the fractional moisture content of the air (B_{wa}) supplied for combustion. (Guidelines for this determination will be discussed later.) The equation for calculating the emission rate is:

$$E = C_w F_w \left[\frac{20.9}{20.9 (1 - B_{wa}) - \%O_{2w}} \right] \quad (3)$$

This equation is a simplification of the theoretically derived equation.[3] Under typical conditions, a positive bias of no more than 0.25 percent is introduced.

The third procedure, the F_c Factor Method, is based on principles related to but slightly different than those for the F_d Factor and F_w Factor Methods:

1. For any given fuel category, a constant ratio exists between the volume of carbon dioxide produced by combustion and the heat content of the fuel. This ratio is called the F_c Factor.
2. The ratio of the theoretical carbon dioxide produced during combustion and the measured carbon dioxide provides an exact basis for dilution correction.

This method requires measurement of the pollutant concentration and percent carbon dioxide ($\%CO_2$) in the effluent stream. Measurements may be made on a wet or dry basis. Using the subscripts, "d" and "w", to denote dry and wet basis measurements, respectively, the equations for calculating E are:

$$E = C_d F_c \left(\frac{100}{\%CO_{2d}} \right) = C_w F_c \left(\frac{100}{\%CO_{2w}} \right) \quad (4)$$

DETERMINATION OF F FACTORS

Values of F_d in dscf/10^6 Btu, F_w in wscf/10^6 Btu, and F_c in scf/10^6 Btu, may be determined on an individual case-by-case basis using the ultimate analysis and gross calorific value of the fuel. The equations are:

$$F_d = \frac{10^6\ (3.64\ \%H + 1.53\ \%C + 0.57\ \%S + 0.14\ \%N - 0.46\ \%O)}{GCV} \qquad (5)$$

$$F_w = \frac{10^6\ (5.57\ \%H + 1.53\ \%C + 0.57\ \%S + 0.14\ \%N - 0.46\ \%O + 0.21\ \%H_2O^*)}{GCV_w}$$

$$F_c = \frac{10^6\ (0.321\ \%C)}{GCV}$$

where: H, C, S, N, O, and H_2O are the concentrations by weight (expressed in percent) of hydrogen, carbon, sulfur, nitrogen, oxygen, and water from the ultimate analysis. (* Note: The $\%H_2O$ term may be omitted if %H and %O include the unavailable hydrogen and oxygen in the form of H_2O.) GCV is the gross calorific value in Btu/lb of the fuel and must always be the value consistent with or corresponding to the ultimate analysis.

For determining F_w, the ultimate analysis and GCV_w must be on an "as received" or "as fired" basis, i.e., it must include the free water. Often in practice, the ultimate analysis and/or gross calorific value of a particular fuel are not known. For most commonly used fuels, tabulated average F Factors may be used instead of the individually determined values. These average values of F_d, F_w, and F_c, calculated from data obtained from the literature,[2-14] are given in Table I. F Factors for wood and bark are also listed in Table I, and factors for various types of refuse are listed in Table II.

ULTIMATE CARBON DIOXIDE

The ratio of F_c to F_d times 100 yields the ultimate percent CO_2 or the maximum CO_2 concentration that the dry flue gas is able to attain. By dividing this number into 20.9, a ratio called the F_o Factor is obtained. F_o values calculated from the ultimate analyses of the various fuels are given in Tables I and II.

F_o values can also be calculated from CO_2 and O_2 data obtained in the field by using the following equation.

$$F_o = \frac{20.9 - \%O_{2d}}{\%CO_{2d}} \quad (8)$$

These calculated F_o values can be used to check Orsat data or other analyses of CO_2 and O_2 that have been adjusted to a dry basis. The process simply involves comparing F_o values calculated from Equation 8 with the values listed in Table I or II. Further details of this validation procedure are outlined in Reference 15.

ERRORS AND APPLICATION

The derivations of Equations 1 through 4 are discussed in References 3, 4, and 5. The following discussion gives further explanation of the F Factors and describes some of the problems and errors that arise in applying the F Factor Methods. Several uses for F Factors in addition to calculating emission rates are outlined.

Deviation in F Factors

The F Factors were calculated from data obtained from the literature. In the October 6, 1975, Federal Register,[2] the values of F_d and F_c were calculated by summing all data points and dividing by the total number of samples. Then the deviations from the extreme values (highest and lowest) were determined. The

higher of the two values, termed "maximum percent deviation from the average F Factors," are listed in parenthesis in Table I. These deviations are probably due to differences in the composition of the fuel, and may also include variations due to the analytical methods and analysts (laboratories). The standard deviations of the samples were not calculated since much of the data were already averages of several samples and there may have been more samples from one locale or of one kind than another.

After publication of the F_d and F_c Factors, it was determined that the midpoint value would be a better value than the average for small samples and for data taken from the literature. Therefore, the F_w Factors and the values for wood and refuse are midpoint values rather than arithmetic averages. The associated deviations are termed, "maximum percent deviation from the midpoint F Factor."

F_w Factors for refuse, wood, and wood bark were not calculated because of the high variability of free moisture contents. For example, the moisture in bark may vary from 20 percent (air dried) to 75 percent (hydraulic debarking).[6] Free moisture content variations of $\pm$ 15 percent introduce about 5 percent variation . However, for lignite, the moisture contents vary only from about 33 to 45 percent. This range causes a deviation of 3.8 percent from the midpoint F_w Factor, which enabled an F_w Factor to be established.

Incomplete Combustion

The assumption of complete combustion is made in the derivation of all F Factor Methods. If products of incomplete combustion, such as carbon monoxide, are present in the effluent stream, the volume of effluent gas and carbon dioxide per pound of fuel burned will differ from the values used in calculating the F Factors. However, adjustments to the measured CO_2 or O_2 concentration can be made, which would minimize the magnitude of the error when applying Equations 1-5.

These adjustments are given by the following equations:

$$(\%CO_2)_{adj} = \%CO_2 + \%CO \quad (9)$$

$$(\%O_2)_{adj} = \%O_2 - 0.5\ \%CO \quad (10)$$

By making these adjustments, the error amounts to minus one-half the concentration of CO present. Thus, if 1 percent CO (an extreme case) is present, an error of minus 0.5 percent is introduced. Without adjusting the CO_2 or O_2 concentration, a combustion source having 11 percent CO_2, 1 percent CO, and 6 percent O_2 will result in about plus 9 percent error for the F_c Factor Method and about plus 3 percent for the F_d Factor and F_w Factor Methods.

Similarly, unburned combustible matter in the ash will cause the volume of effluent gas and carbon dioxide per unit of heat input to differ from the calculated F Factor values. This is true, however, only if the heat input is thought of in terms of the coal input rate times the calorific value. If the heat input rate is considered as only that calorific value which is derived from the combusted matter, the F Factor Methods are only slightly affected. In other words, if any portion of the fuel goes through the combustion process unburned, the F Factor Methods will not include as heat input the calorific value associated with the uncombusted matter, and a slight positive bias will be introduced.

The positive bias is due to the combustion process, which is said to consist first of evaporating the free moisture, then the burning of the volatile matter, and last the burning of the fixed carbon, with the ash remaining. The volatile matter includes hydrogen, which results in a lower F Factor than the calculated values. Since a higher proportion of fixed carbon than volatile matter generally remains in the ash, the F_c Factor Method is affected more than the F_d Factor and

F_w Factor Methods. For example, assume that 100 lb of a coal, which has 55 8% C, 5.7% H, 1.1% N, 3.2% S, 21.5% O, and 12.6% ash (percent by weight, as received basis), is burned and 5 lb fixed carbon remains in the ash. About plus 2.3 percent error is incurred with the F_c Factor and less than 1 percent with the F_d Factor and F_w Factor Methods.

Effect of Wet Scrubbers

When wet scrubbers are used, a portion of the carbon dioxide may be absorbed by the scrubbing solution. Therefore, the F_c Factor Method will yield an emission rate higher than the actual rate. If a gas stream having 14% CO_2 before the scrubber loses 10 percent of the CO_2, or 1.4% CO_2, the error is about plus 13 percent.

The F_d Factor Method is also affected by the loss of CO_2 in the scrubber, but to a lesser degree than the F_c Factor Method. If the gas stream has 6% O_2 and 1.4% CO_2 is lost in the scrubber, the error will be about plus 2 percent.

The F_w Factor Method is not applicable after wet scrubbers since the scrubber generally adds moisture to the flue gas, thereby "diluting" the gas stream. The pollutant concentration will be lowered by the same proportion of moisture added and the O_2 concentration will be lower than actual, which would tend to yield lower than true numbers.

When the scrubbing solution is lime or limestone, the F_c Factor Method may be used after wet scrubbers. It is generally assumed that due to the optimum operating conditions, the amount of CO_2 absorption is minimized and, therefore, the application of the F_c Factor Method will not yield appreciable errors. However, with limestone scrubbers, there is a possibility of CO_2 being added to the gas stream due to the reaction of SO_2 with the limestone. Therefore, the F_c Factors must be increased by 1 percent.

Determination of Ambient Air Moisture

Guidelines have been developed for the determination of B_{wa}, the moisture fraction in ambient air, in Equation 3, which will soon be published in the Federal Register. The guidelines are presented below.

Approval may be given for determination of B_{wa} by on-site instrumental measurement provided that the absolute accuracy of the measurement technique can be demonstrated to be within $\pm$ 0.7 percent water vapor. In lieu of actual measurement, B_{wa} may be estimated as follows: (Note that the following estimating factors are selected to assure that any negative error introduced in the emissions by the estimating term $\frac{20.9}{20.9\ (1 - B_{wa}) - \%O_{2ws}}$ will not be larger than -1.5 percent. However, positive errors, or over-estimation of emissions, of as much as 5 percent may be introduced depending upon the geographic location of the facility and the associated range of ambient moisture.)

1. B_{wa} = 0.027. This factor may be used as a constant value at any location.
2. B_{wa} = highest monthly average of B_{wa} that occurred within a calendar year at the nearest Weather Service Station, calculated using data for the past 3 years. This factor may be used on an annual basis at any facility.
3. B_{wa} = highest daily average of B_{wa} that occurred within a calendar month at the nearest Weather Service Station, calculated for each month for the past 3 years used as an estimating factor for the respective calendar month.

Sampling Location and Sampling Points

Ambient air leakage into an exhaust system may cause variations across the duct or stack in the relative concentrations of CO_2 and O_2. For this reason, the Federal regulations[2] specify that CO_2 or O_2 be measured simultaneously and approximately at the same point as the gaseous pollutants measurements.

For particulate emission performance tests, which require traversing, it is specified that the O_2 samples be obtained simultaneously by traversing the duct at the same sampling location used for each run of the Method 5. This requirement may be satisfied by attaching a stainless steel tube to the particulate sampling probe and, using a small diaphragm pump, obtaining an integrated gas sample over the duration of the run (of Reference 1). The sample should be analyzed using an Orsat apparatus.

As an alternative to traversing the same sampling points of Method 5, a minimum of 12 oxygen sampling points may be used for each run. This would require a separate integrated gas sampling train traversing the duct work simultaneously with the particulate run.

Other Applications

In addition to calculating emission rates, F Factors have several other uses. If Q_{sd}, the dry effluent volumetric flow rate, or Q_{sw}, the wet effluent volumetric flow rate, and Q_H, the heat input rate, are measured, a value of F_d, F_w, or F_c may be calculated. These equations are given below:

$$F_{d(calc)} = \frac{Q_{sd}}{Q_H} \frac{20.9 - \%O_2}{20.9} \quad (11)$$

$$F_{w(calc)} = \frac{Q_{sw}}{Q_H} \frac{20.9\ (1 - B_{wa}) - \%O_{2w}}{20.9} \quad (12)$$

$$F_{c(calc)} = \frac{Q_{sd}}{Q_H} \frac{\%CO_{2d}}{100} = \frac{Q_{sw}}{Q_H} \frac{\%CO_{2w}}{100} \quad (13)$$

The calculated values may then be compared to tabulated values of the F Factors to facilitate a material balance check.

If desired, Q_H can be calculated by using the Equations 11 through 13. In the past, it has been observed that the measurement of Q_s has been significantly greater than the stoichiometric calculations rates. The discrepancy is usually due to errors in determining Q_s. Due to aerodynamic interferences and improper alignment of the pitot tubes, higher than real readings have been obtained. Therefore, errors in measuring Q_s are positive, which leads to higher than true firing rates.

If an ultimate analysis and calorific determination of a particular fuel are made and the F Factor value is calculated, the accuracy of the results may be checked by comparison with the tabulated F Factors.

SUMMARY

The various F Factor Methods have been summarized and calculated F Factors for fossil fuels, wood, wood bark, and refuse material have been presented. In addition, some of the problems and errors that arise in applying the F Factor Method for calculating power plant emission rates were discussed and other uses of the F Factors were outlined.

TABLE I. F FACTORS FOR VARIOUS FUELS[2-14,a,b,c]

Fuel Type	F_d dscf/10^6 Btu	F_w wscf/10^6 Btu	F_c scf/10^6 Btu	F_o
Coal				
Anthracite	10140 (2.0)	10580 (1.5)*	1980 (4.1)	1.070 (2.9)
Bituminous	9820 (3.1)	10680 (2.7)	1810 (5.9)	1.140 (4.5)
Lignite	9900 (2.2)	12000 (3.8)	1920 (4.6)	1.076 (2.8)
Oil	9220 (3.0)	10360 (3.5)	1430 (5.1)	1.346 (4.1)
Gas				
Natural	8740 (2.2)	10650 (0.8)	1040 (3.9)	1.749 (2.9)
Propane	8740 (2.2)	10240 (0.4)	1200 (1.0)*	1.510 (1.2)*
Butane	8740 (2.2)	10430 (0.7)	1260 (1.0)	1.479 (0.9)
Wood	9280 (1.9)*	----------	1840 (5.0)	1.050 (3.4)
Wood Bark	9640 (4.1)	----------	1860 (3.6)	1.056 (3.9)

a Numbers in parenthesis are maximum deviations (%) from either the midpoint or average F Factors.

b To convert to metric system, multiply the above values by 1.123×10^{-4} to obtain scm/10^6 cal.

c All numbers below the asterisk (*) in each column are midpoint values. All others are averages.

TABLE II. MIDPOINT F FACTORS FOR REFUSE[2-14,a,b]

	F_d dscf/10^6Btu	F_c wscf/10^6Btu	F_o
Paper and Wood Wastes[c]	9260 (3.6)	1870 (3.3)	1.046 (4.6)
Lawn and Garden Wastes[d]	9590 (5.0)	1840 (3.0)	1.088 (2.4)
Plastics			
Polyethylene	9173	1380	1.394
Polystyrene	9860	1700	1.213
Polyurethane	10010	1810	1.157
Polyvinyl chloride	9120	1480	1.286
Garbage[e]	9640 (4.0)	1790 (7.9)	1.110 (5.6)
Miscellaneous			
Citrus rinds and seeds	9370	1920	1.020
Meat scraps, cooked	9210	1540	1.252
Fried fats	8939	1430	1.310
Leather shoe	9530	1720	1.156
Heel and sole composition	9480	1550	1.279
Vacuum cleaner catch	9490	1700	1.170
Textiles	9354	1840	1.060
Waxed milk cartons	9413	1620	1.040

a Numbers in parentheses are maximum deviations (%) from the midpoint F Factors.

b To convert to metric system, multiply the above values by 1.123×10^{-4} to obtain scm/10^6 cal.

c Includes newspapers, brown paper, corrugated boxes, magazines, junk mail, wood, green logs, rotten timber.

d Includes evergreen shrub cuttings, flowing garden plants, leaves, grass.

e Includes vegetable food wastes, garbage (not described).

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VALIDATING ORSAT ANALYSIS DATA FROM FOSSIL-FUEL-FIRED UNITS

R. T. Shigehara, R. M. Neulicht, and W. S. Smith

INTRODUCTION

In the September 11, 1974 Federal Register,[1] a new reference method for calculating the pollutant emissions from fossil fuel-fired steam - generating units of more than 250 million Btu/hr heat input was proposed. This proposed method is based on the law of conservation of mass and energy and utilizes oxygen (O_2) concentration to compensate for excess or dilution air.[2] Recently, another method has been published[3] that uses the same principle, except that carbon dioxide (CO_2) concentration is used to adjust for excess or dilution air.

The validity of both methods relies heavily on the accuracy of either the O_2 or CO_2 measurement. Therefore, it is desirable to have some criteria for validating the data as soon as they are obtained in the field. Since, in many cases, both O_2 and CO_2 measurements are obtained from Orsat analyses, guidelines are given for validating the data from these analyses.

CO_2-O_2 RELATIONSHIP

Since air is used for the combustion process, the law of conservation of mass demands that:

$$\%O_2 + F_o \%CO_2 = 20.9 \qquad (1)$$

where: $\%O_2$ = O_2 content by volume (expressed as percent), dry basis

$\%CO_2$ = CO_2 content by volume (expressed as percent), dry basis

F_o = fuel factor; depends on the type of fuel burned

20.9 = O_2 content in air by volume (expressed as percent), dry basis.

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Solving for F_o, we obtain:

$$F_o = \frac{20.9 - \%O_2}{\%CO_2} \qquad (2)$$

The factor F_o is mainly a function of the hydrogen (H) to carbon (C) ratio in the fuel.[4] At zero percent excess air (i.e., when fuel is burned completely with stoichiometric amount of air), Equation 2 simplifies to:

$$F_o = \frac{20.9}{(\%CO_2)_{ult}} \qquad (3)$$

where $(\%CO_2)_{ult}$ is the ultimate CO_2 or the maximum CO_2 concentration that the dry flue gas is able to attain. Given the ultimate analysis of the fuel being burned, this value can be calculated by using the following equation:[5]

$$(\%CO_2)_{ult} = \frac{0.321\ \%C\ (100)}{1.53\ \%C + 3.64\ \%H + 0.57\ \%S + 0.14\ \%N - 0.46\ \%O} \qquad (4)$$

where %C, %H, %S, %N, and %O are the percent by weight of carbon, hydrogen, sulfur, nitrogen, and oxygen, respectively, obtained from the ultimate analysis.

Equations 1 through 4 can be used to check Orsat data or other analyses of CO_2 and O_2 that have been adjusted to a dry basis. The process simply involves comparing F_o values calculated from Orsat analyses (Equation 2) with F_o values calculated from the ultimate analyses of the fuels being burned (Equations 3 and 4). Alternatively, a graphical approach may be used. With CO_2 as the abscissa and O_2 as the ordinate on arithmetic paper (see Figure 1), a straight line drawn between 20.9% O_2 and the ultimate CO_2 calculated from the ultimate analysis (Equation 4) represents Equation 1. The Orsat analysis

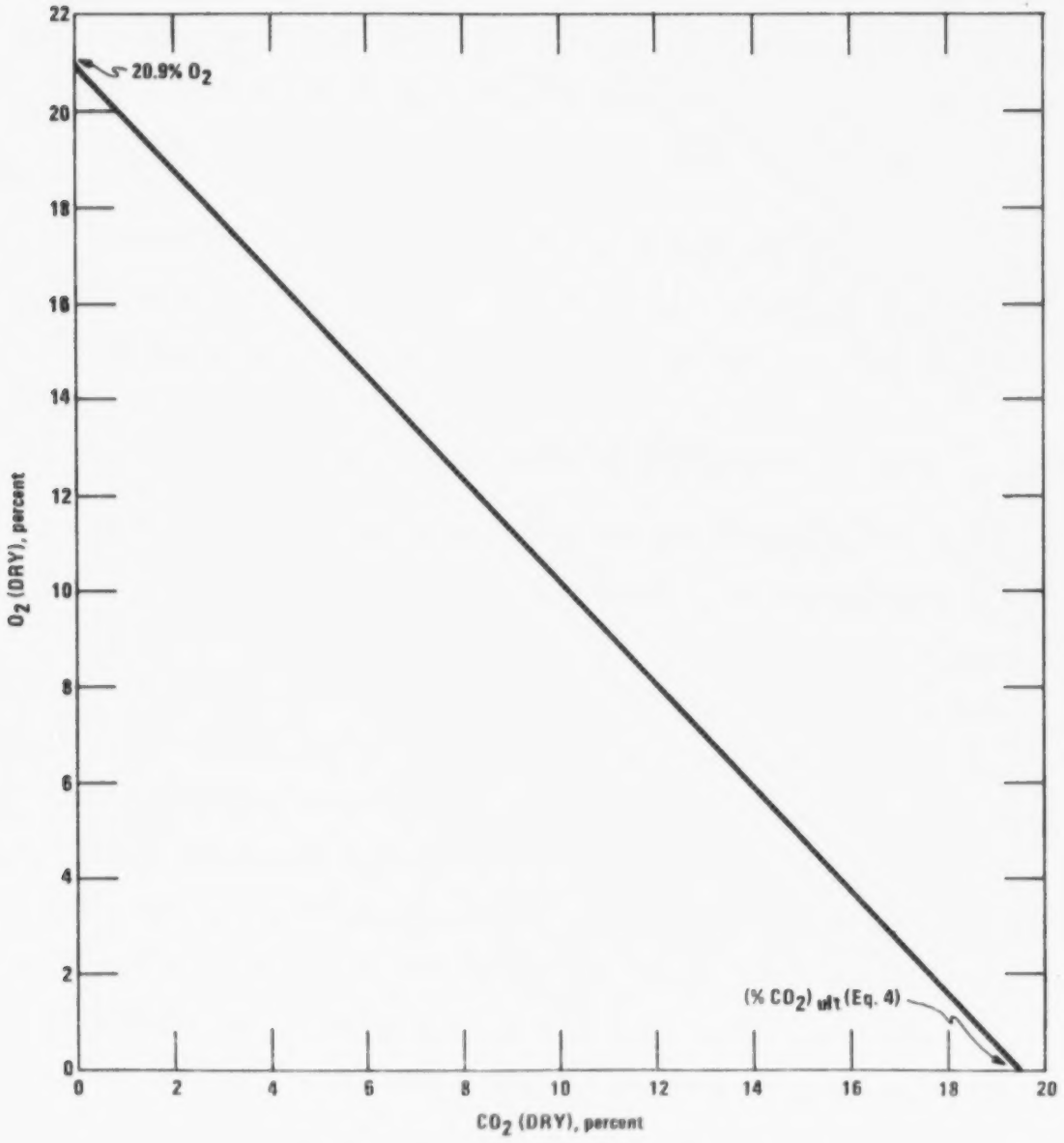

Figure 1. Graph construction for checking Orsat data.

is checked by plotting the data points on this graph.

Equation 1 or 2 assumes complete combustion of the fuel. If carbon monoxide (CO) is present in measurable quantities, the O_2 and CO_2 must be adjusted when using the equations as follows:

$$(\%CO_2)_{adj} = \%CO_2 + \%CO \quad (5)$$

$$(\%O_2)_{adj} = \%O_2 - 0.5\ \%CO \quad (6)$$

Since the method of validating Orsat analyses is based on combustion of fossil fuel and dilution of the gas stream with air, this method will not be applicable to sources that (1) remove CO_2 (e.g., sources that use wet scrubbers) or O_2, or (2) add O_2 and N_2 in a proportion different from that of air or (3) add CO_2 (e.g., cement kilns).

SUMMARY OF AVERAGE F_o FACTORS AND ULTIMATE CO_2'S

When ultimate analyses of the fuel being burned are not available, averages may be used. Table I summarizes F_o factors and ultimate CO_2's and their averages for various type fuels based on ultimate analyses reported in the literature.[6-15] Some of the average F_o factors and $(\%CO_2)_{ult}$ were calculated by use of a small number of samples. It is recommended, therefore, that the data be updated by users as more information becomes available. The manner in which these averages can be used to validate Orsat data will be explained later.

F_o and ULTIMATE CO_2 TOLERANCES

As mentioned earlier, the purpose for the O_2 or CO_2 measurements is primarily to adjust the pollutant concentrations for dilution air. In

Table I F_o Factors for Fossil Fuels[a]

Fuel type	Literature source	Number of samples	Average F_o	$(\% CO_2)_{ult}$	Maximum Deviation, % +	-
Coal						
Anthracite	6	3	1.0786	19.38		
	7	1	1.0525	19.86		
	8	3	1.0671	19.59		
Overall avg.			1.0699	19.53	2.9	2.3
Bituminous	8	13	1.1202	18.66		
	9	38	1.1407	18.32		
	10	13	1.1336	18.44		
	11	39	1.1450	18.25		
	12	26	1.1435	18.28		
Overall avg.			1.1398	18.34	3.6	4.5
Lignite	8	1	1.0779	19.39		
	6	1	1.0791	19.37		
	16	198	1.0761	19.42		
Overall avg.			1.0761	19.42	2.8	2.8
Oil						
Crude	7	1	1.3628	15.34		
	14	6	1.3561	15.41		
Residium	14	4	1.3280	15.74		
Distillate	14	2	1.3464	15.52		
Overall avg.			1.3465	15.52	2.9	4.1
Gas						
Natural	15	4	1.7594	11.88		
	6	3	1.7349	12.05		
Overall avg.			1.7489	11.95	1.8	2.9
Propane	15	2	1.5095	13.85		
Overall avg.			1.5095	13.85	1.2	1.2
Butane	15	2	1.4791	14.13		
Overall avg.			1.4791	14.13	0.9	0.9

[a] Standard conditions are 70°F, 29.92 in. Hg, and 0% excess air.

evaluating the effect of the inaccuracy of the measurement on the final result, it is important to consider not only the O_2 and CO_2 relationship, but also the level of their concentrations. An explanation follows.

The adjustment factors for dilution air are:

$$F_{do} = \frac{20.9 - K_o}{20.9 - \%O_2} \quad (7)$$

$$F_{dc} = \frac{K_c}{\%CO_2} \quad (8)$$

where: F_{do} and F_{dc} = adjustment factors for dilution air based on O_2 and CO_2, respectively

K_o and K_c = reference O_2 and CO_2 concentrations, respectively

$\%O_2$ and $\%CO_2$ = percent by volume of O_2 and CO_2, respectively, dry basis

20.9 = percent by volume of O_2 in air, dry basis.

The relative errors introduced in the adjustment factors by inaccuracies of the O_2 and CO_2 measurement can be approximated by the following equations (also shown graphically in Figure 2):

$$E_{do} = \frac{d(\%O_2)}{20.9 - \%O_2} \times 100 \quad (9)$$

$$E_{dc} = \frac{d(\%CO_2)}{\%CO_2} \times 100 \quad (10)$$

where: E_{do} and E_{dc} = relative errors introduced in the adjustment factors based on O_2 and CO_2, respectively, percent

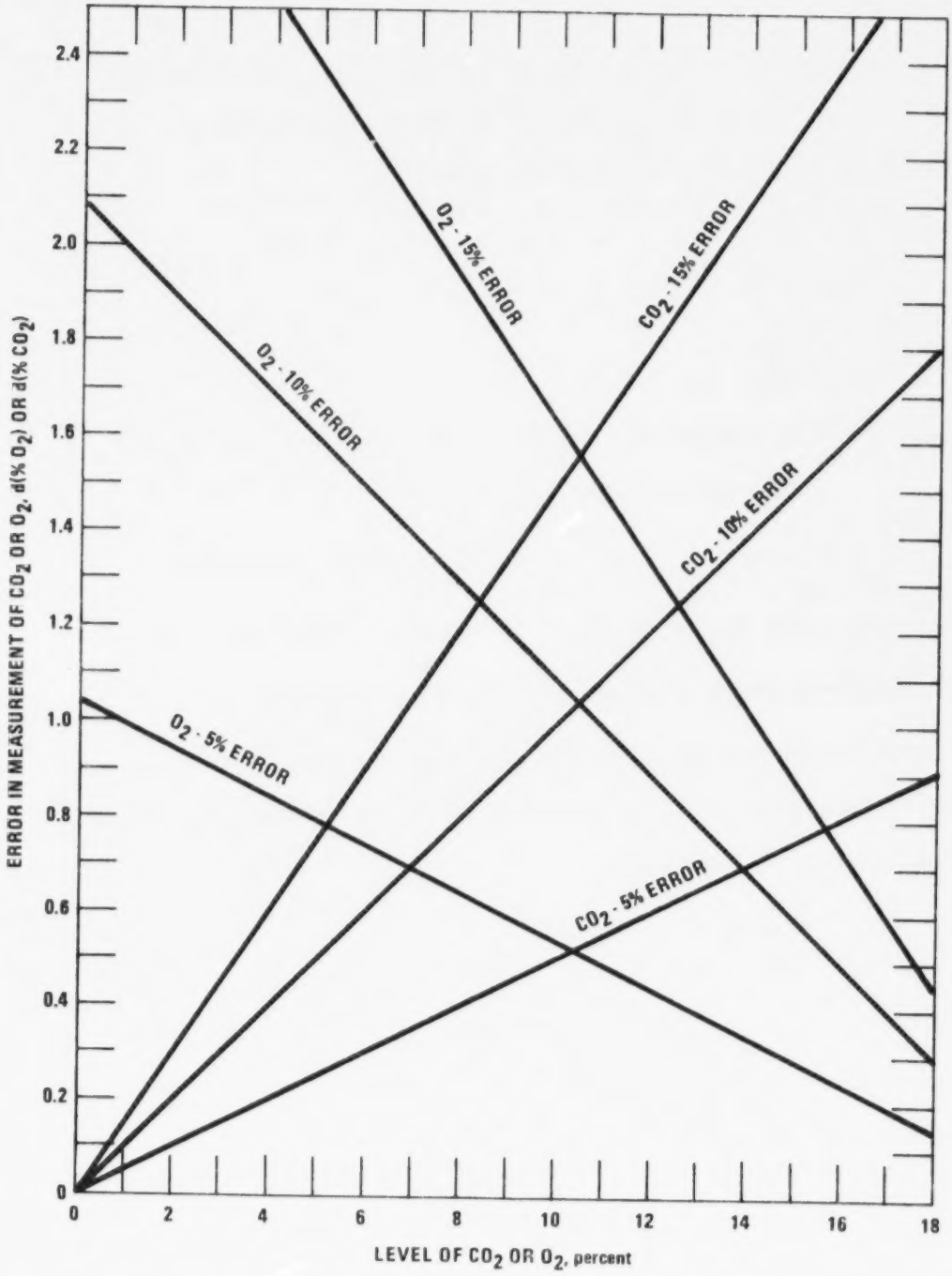

Figure 2. Relative errors resulting from inaccurate CO_2 or O_2 measurements.

$d(\%O_2)$ and $d(\%CO_2)$ = deviation from the true value of O_2 and CO_2, respectively, percent by volume.

If $d(\%O_2)$'s and $d(\%CO_2)$'s can be determined or estimated, Figure 2 can be valuable in making decisions or evaluations. For example, if the CO_2 level is about 12 to 14%, Fyrites* that are capable of measuring CO_2 to within 0.5% would be adequate for making F_{dc} calculations. If the CO_2 concentration is down at the 2% level, however, it can be seen that to achieve, for example, a 5% accuracy, a measurement to within 0.1% CO_2 is required. Thus, Orsats with burettes capable of measuring to within 0.1% CO_2, not Fyrites, should be used.

To estimate the tolerances of F_o and the ultimate CO_2 for a desired accuracy of E_{do} or E_{dc}, the following relationship is helpful:

$$\frac{dF_o}{F_o} = \frac{d(\%CO_2)_{ult}}{(\%CO_2)_{ult}} = \left[- \frac{d(\%O_2)}{20.9 - \%O_2} - \frac{d(\%CO_2)}{\%CO_2} \right] = - \left[\frac{(E_{do} + E_{dc})}{100} \right] \qquad (11)$$

Equation 11 shows that the tolerance of F_o or $(\%CO_2)_{ult}$ is the sum of E_{do} and E_{dc}. With the understanding that E_{do} and E_{dc} can be a range of plus or minus values, however, the tolerance of F_o or $(\%CO_2)_{ult}$ must be limited to the same magnitude of E_{do} or E_{dc} to ensure that E_{do} or E_{dc} will be less than that magnitude. For example, to limit E_{do} or E_{dc} to $\pm$ 5%, F_o or $(\%CO_2)_{ult}$ must also be limited to $\pm$ 5%.

PROCEDURE

Based on the previous discussion, the following procedure can be established for validating Orsat analysis data:

* Trade name; not to be considered an endorsement.

1. Decide tolerances for E_{do} or E_{dc}.

2. If ultimate analysis of fuel being burned is available, calculate F_o using Equations 3 and 4 or $(\%CO_2)_{ult}$ using Equation 4. Otherwise, use average values from Table I. Then calculate the limits of tolerance for F_o or $(\%CO_2)_{ult}$. For example, if a $\pm$ 5% tolerance is desired, the tolerance limits would be 0.95 and 1.05 times the calculated F, or (% CO_2) ult. Construct graphs as in Figure 1, using these tolerance limits.

3. To compare field Orsat data, calculate F_o, using Equation 2, or plot the data points on the graph. Values beyond the established tolerance levels should be rejected and the analysis run over.

If average values, rather than the ultimate analysis of the fuel being burned, serve as the basis of comparison, it should be understood that there may be exceptions. If repeated Orsat analyses, including a double-check of the Orsat apparatus and analyses run by another person, consistently yield values that are rejected, the average values should be considered suspect and the Orsat analyses accepted.

A graphical nomograph technique using a $\pm$ 5% tolerance level and average values from Table I is shown in Figure 3.

SUMMARY

For any given fuel burned with air, a relationship between O_2 and CO_2 must exist. This relationship can be used to advantage to validate Orsat analysis data. On the basis of ultimate analysis or average values of F_o or $(\%CO_2)_{ult}$ calculated from data in the literature, a procedure has been presented for validating Orsat analysis data.

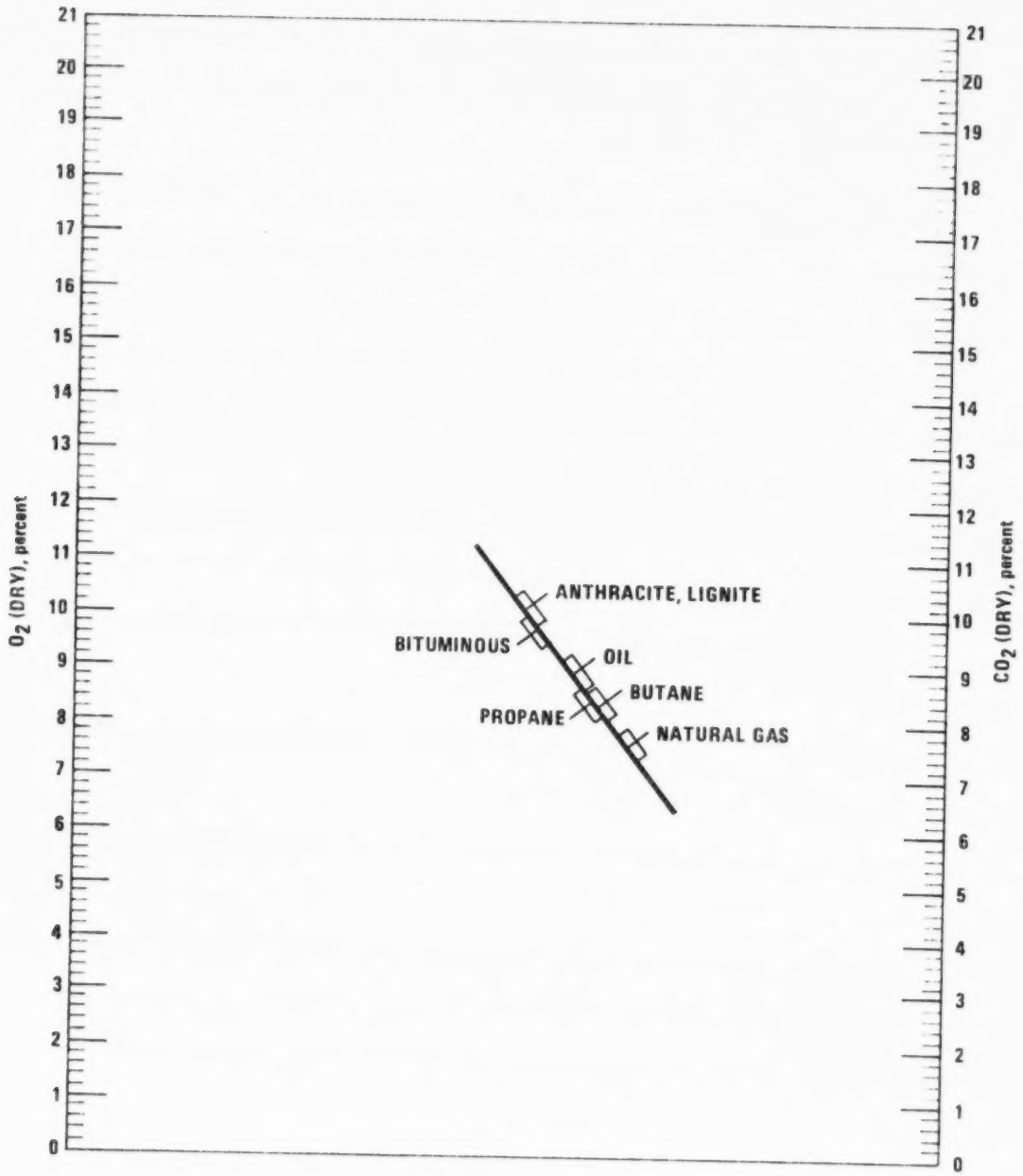

Figure 3. Nomograph for checking Orsat data ± 5% in E_{do} or E_{dc}.

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A GUIDELINE FOR EVALUATING COMPLIANCE TEST RESULTS

(Isokinetic Sampling Rate Criterion)

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Introduction

The sampling rate used in extracting a particulate matter sample is important because anisokinetic conditions can cause sample concentrations to be positively or negatively biased due to the inertial effects of the particulate matter. Hence, the calculation of percent isokinetic (I) is a useful tool for validating particulate test results. Section 6.12 of the recently revised Method 5[1] states, "If 90 percent $\leq$ I $\leq$ 110 percent, the results are acceptable. If the results are low in comparison to the standard and I is beyond the acceptable range, or, if I is less than 90 percent, the Administrator may opt to accept the results."

This guideline provides a more detailed procedure on how to use percent isokinetic to accept or reject test results when the sampling rate is beyond the acceptable range. The basic approach of the procedure is to account for the inertial effects of particulate matter and to make a maximum adjustment on the measured particulate matter concentration.[2] Then, after comparison with the emission standard, the measured particulate matter concentration is categorized (1) as clearly meeting or exceeding the emission standard or (2) as being in a "gray area" zone. In the former category, the test report is accepted; in the latter, a retest should be done because of anisokinetic sampling conditions.

Procedure

1. Check or calculate the percent isokinetic (I) and the particulate

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matter concentration (c_s) according to the procedure outlined in Method 5. Note that c_s must be calculated using the volume of effluent gas actually sampled (in units of dry standard cubic feet, corrected for leakage). Calculate the emission rate (E), i.e. convert c_s to the units of the standard. For the purposes of this guideline, it is assumed that all inputs for calculating E are correct and other specifications of Method 5 are met.

2. Compare E to the standard. Then accept or reject c_s using the criteria outlined below. (A summary is given in Table I):

a. Case 1 - I is between 90 and 110 percent. The concentration c_s must be considered acceptable. A variation of $\pm$ 10 percent from 100 percent isokinetic is permitted by Method 5.

b. Case 2 - I is less than 90 percent.

(1) If E meets the standard, c_s should be accepted, since c_s can either be correct (if all particulate matter are less than about 5 micrometers in diameter) or it can be biased high (if larger than 5 micrometer particulate matter is present) relative to the true concentration; one has the assurance that c_s is yielding an E which is definitely below the standard.

(2) If E is above the standard, multiply c_s by the factor (I/100) and recalculate E. If, on the one hand, this adjusted E is still higher than the standard, the adjusted c_s should be accepted; a maximum adjustment which accounts for the inertial effects of particulate matter has been made and E still exceeds the standard. On the other hand, if the

adjusted E is lower than the standard, a retest should be done.

c. Case 3 - I is greater than 110 percent.

(1) If E exceeds the standard, c_s should be accepted, since c_s can either be equal to the true concentration or biased low relative to it; one has the assurance that E is definintely over the standard.

(2) If E is below the standard, multiply c_s by the factor (I/100) and recalculate E. If, on the one hand, this adjusted E is still lower than the standard, the adjusted c_s should be accepted; a maximum adjustment which accounts for the inertial effects of particulate matter has been made and E still meets the standard. On the other hand, if the adjusted E exceeds the standard, a retest should be done.

Table I. Summary of Procedure

Case	I	Category	Decision
1	90 - 110		Accept
2	< 90	$E \leq$ Em. Std.	Accept
		$c_s(I/100) \rightarrow E_{adj} >$ Em. Std.	Accept
		$c_s(I/100) \rightarrow E_{adj} \leq$ Em. Std.	Retest
3	> 110	E > Em. Std.	Accept
		$c_s(I/100) \rightarrow E_{adj} \leq$ Em. Std.	Accept
		$c_s(I/100) \rightarrow E_{adj} >$ Em. Std.	Retest

Summary

A procedure for accepting or rejecting particulate matter test results based on percent isokinetic has been outlined. It provides a mechanism for accepting all data except where anisokinetic sampling might affect the validity of the test results. This procedure is one of several useful tools for evaluating testing results.

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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

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15. SUPPLEMENTARY NOTES

16. ABSTRACT

"Stack Sampling Technical Information" is a four-volume collection of monographs and papers which have been compiled by the Emission Measurement Branch, ESED, OAQPS. The information specifically relate to current EPA test methods and compliance test procedures. The data presented in some of these documents have served as the basis for a number of revisions made in the EPA Reference Methods 1 through 8. Several of the documents are also useful in determining acceptable alternative procedures.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Gas Sampling Filtered Particle Sampling Gas Analysis	Stack Sampling	14B 14D

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